(19) World Intellectual Property Organization International Bureau



(43) International Publication Date 17 January 2002 (17.01.2002)

PCT

(10) International Publication Number WO 02/04357 A1

(51) International Patent Classification⁷: C02F 1/469, B01D 61/48, B01J 47/08

(21) International Application Number: PCT/GB01/02967

(22) International Filing Date: 5 July 2001 (05.07.2001)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data: 0016846.8

10 July 2000 (10.07.2000) G

(71) Applicant (for all designated States except US): VIVENDI WATER SYSTEM LIMITED [GB/GB]; Protean House, High Street, Lane End, High Wycombe HP14 3JH (GB).

(72) Inventors; and

(75) Inventors/Applicants (for US only): EMERY, Nigel, Philip [GB/GB]; 10a Roberts Road, High Wycombe, Buckinghamshire HP13 6XA (GB). WHITEHEAD, Paul [GB/GB]; Mill Lane Cottage, Mill Lane, Henley on Thames, Oxon RG9 4HB (GB). WOODWARD, Roger, John [GB/GB]; Cedars, 64 Green Lane, Radnage, High Wycombe, Buckinghamshire (GB).

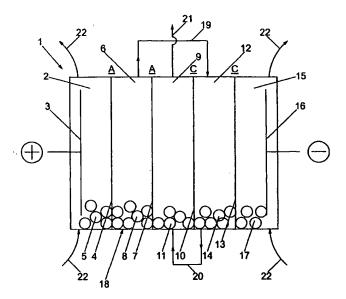
- (74) Agent: MURGITROYD & COMPANY; 373 Scotland Street, Glasgow G5 8QA (GB).
- (81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.
- (84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:

- with international search report

[Continued on next page]

(54) Title: ELECTRODEIONISATION APPARATUS



(57) Abstract: An electrodeionisation apparatus comprising, successively: means defining an anode chamber, means defining one or more anion exchange chambers, means defining one or more mixed exchange chambers, means defining one or more cation exchange chambers, and means defining a cathode chamber, the anion, mixed and cation exchange chambers providing a flow path for water to be purified, is described. The present invention incorporates advantages of both separate resin bed and mixed resin bed technology.



VO 02/04357 A



 before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

1

1	Electrodeionisation Apparatus
2	•
3	The present invention relates to an
4	electrodeionisation apparatus for purifying water
5	and method therefor.
6	
7	Apparatus and methods for electrodeionisation to
. 8	provide purified water are well known, see for
9	example our GB-A-2311999 and US 4687561. Generally,
10	water to be purified is passed along a deionising
11	path set between an anode and a cathode. The
12	application of a potential difference between the
13	anode and cathode causes anions and cations in the
14	impure water to migrate towards their respective
15	attracting electrodes through perm-selective
16	membranes.
17	
18	In general, such apparatus has the chambers for
19	exchanging anions and cations juxtapositioned so
20 ·	that the anions and cations removed from the water
21	being purified both travel towards one or more
22	'concentrating' chambers, through which a desalting

2

stream flows to remove the unwanted anions and 1 2 . cations. 3 It is an object of the present invention to provide 4 a simplified electrodeionisation apparatus and 5 6 method. 7 According to one aspect of the present invention, 8 9 there is provided an electrodeionisation apparatus comprising, successively: 10 11 12 means defining an anode chamber, means defining one or more anion exchange chambers, 13 means defining one or more mixed exchange chambers, 14 15 means defining one or more cation exchange chambers, 16 and 17 means defining a cathode chamber, 18 the anion, mixed and cation exchange chambers 19 providing a flow path for water to be purified. 20 21 By locating the or each anion exchange chamber next 22 to the anode chamber, and locating the or each 23 cation exchange chamber next to the cathode chamber, 24 the apparatus of the present invention provides an 25 opposite or reverse flow-path for exchanged anions 26 and cations than prior apparatus. The exchanged 27 anions and cations in the water being purified are 28 29 directly attracted to neighbouring electrodes, rather than being attracted to distal electrodes . 30 located across opposing exchange chambers of prior 31 32 electrodeionisation apparatus.

3

1 In one embodiment of the present invention, the 2 apparatus involves one anion exchange chamber and 3 one cation exchange chamber. 4 5 Located between the chambers are perm-selective 6 membranes as are known in the art. Those membranes 7 located between the or each central mixed exchange 8 chamber and the cathode chamber should be cation 9 membranes, and those membranes located between the 10 or each mixed exchange chamber and the anode chamber 11 should be anion membranes. 12 13 Preferably, the or each anion exchange chamber 14 partly, substantially or wholly contains anion 15 exchange material, and the or each cation exchange 16 chamber partly, substantially or wholly contains 17 cation exchange material. 18 19 Preferably, the anode chamber partly, substantially or wholly contains ion exchange material, preferably 20 21 cation exchange material. Preferably, the cathode 22 chamber, partly, substantially or wholly contains 23 ion exchange material, more preferably cation 24 exchange material. Also preferably, the or each 25 mixed exchange chamber partly, substantially or 26 wholly contains mixed ion exchange material. exchange materials are known in the art, one example 27 28 being resin beads. 29 30 The anode and cathode chambers are preferably flushed with a desalting stream such as water to 31 32 elute ions from the system as concentrate.

4

In another embodiment of the present invention, 1 water to be purified is firstly passed through an 2 anion exchange chamber of the apparatus, then 3 through a cation exchange chamber, and subsequently 4 through a mixed exchange chamber. 5 6 Alternatively, water to be purified is passed 7 through a cation exchange chamber, then through an 8 anion exchange chamber, and subsequently through a 9 mixed exchange chamber. 10 11 Where apparatus of the present invention involves 12 two or more anion exchange chambers and/or two or 13 more cation exchange chambers and/or two or more 14 mixed exchange chambers, then impure water flow path 15 could be directed through subsequent anion exchange 16 .17 chambers and/or subsequent cation exchange chambers and/or subsequent mixed exchange chambers in the · 18 same or any suitable or relevant order. 19 20 In a third embodiment of the present invention, 21 water to be purified by the present apparatus is 22 combined with already purified water, so reducing, 23 by dilution, the load on the exchange materials. 24 The already purified water may be provided from a 25 separate source, or be provided by re-circulating 26 27 outflow from the present apparatus, which outflow could be temporarily held in a reservoir such as a 28 29 holding tank. 30 31 According to a fourth embodiment of the present invention, the anion, cation and mixed exchange 32

5

1 chambers are relatively thick compared with chambers 2 of prior art electrodeionisation apparatus. 3 simplicity of the present invention allows thicker chambers and beds of ion exchange materials to be 4 5 used, compared with the conventional view that 6 thinner beds are necessary to maintain electric . 7 current flow thereacross. 8 9 The present invention also extends to a 'multiple' 10 unit still only involving one set of electrodes. 11 For example, the unit could be arranged: anode 12 (chamber), anion, mixed, cation, concentrate..., anion, mixed, cation, concentrate..., anion, mixed, 13 14 cation, cathode. 15 16 According to a second aspect of the present invention, there is provided a method of 17 18 electrodeionisation comprising causing or allowing 19 water to be purified to flow through an anion 20 exchange chamber neighbouring an anode chamber, 21 followed by flow through a cation exchange chamber 22 neighbouring a cathode chamber, or vice versa, 23 followed by flow through a mixed exchange chamber 24 located between the anion exchange chamber and the 25 cation exchange chamber. 26 27 The method of the present invention could use 28 electrodeionisation apparatus as described above. 29 In the method of the present invention, the water to 30 be purified could be pre-mixed with a proportion of 31 already purified water. 32

6

1 In general, water may be passed through each chamber 2 independently, allowing different flow rates, 3 including no flow, at different times. 4 An embodiment of the present invention will now be 5 6 described by way of example only, and with reference 7 to the accompanying drawing, Figure 1, which is a schematic cross-sectional side view of apparatus 8 according to the present invention. 9 10 Referring to the drawing, Figure 1 shows an 11 electrodeionisation apparatus in the form of a stack 12 (1). The stack (1) has five chambers. The first 13 chamber (2) is an anode chamber bounded on one side 14 by an anode (3) and on the other by an anion 15 16 membrane (4). The anode chamber (2) contains cation 17 exchange resin beads (5). Juxtaposed the anode 18 chamber (2) is an anion exchange chamber (6) bounded on one side by the anion membrane (4), and on the 19 20 other side by a second anion membrane (7). anion exchange chamber (6) contains anion exchange 21 resin beads (8). Next to the anion exchange chamber 22 (6) is a mixed exchange chamber (9), bounded by the 23 24 second anion membrane (7) and a cation membrane (10). This chamber (9) contains mixed ion exchange 25 26 resin beads (11). 27 Juxtaposed the mixed exchange chamber (9), there is 28 a cation exchange chamber (12) bounded by the cation 29 membrane (10), and a second cation membrane (13). 30 The cation exchange chamber (12) contains cation 31 32 exchange resin beads (14).

7

Juxtaposed the cation exchange chamber (12) lies a 1 cathode chamber (15) bounded by the second cation 2 3 exchange membrane (13) and a cathode (16). cathode chamber (15) contains cation exchange resin 4 5 (17).6 The nature and form of the electrodes, membranes and 7 ion exchange materials are all known in the art. 8 9 10 In use, impure feed water (18) enters the stack (1), 11 and firstly enters the anion exchange chamber (6). The anion exchange resin beads (8) in this chamber 12 (6) replace the anions in the feed water with 13 hydroxide ions from the resin beads (8). The anions 14 then move towards and through the anion exchange 15 membrane (4) to the anode chamber (2). The driving 16 force for this movement is an electrical potential 17 placed between the anode (3) and cathode (16). 18 feed water (19) exiting this chamber (6) is then 19 passed into the cation exchange chamber (12), where 20 the cation exchange resin beads (14) exchange 21 cations in the feed water for hydrogen ion. 22 23 cations then move towards and through the cation exchange membrane (13) to the cathode chamber (15). 24 25 26 The water (20) exiting this chamber (12) is then 27 passed into the mixed resin chamber (9). resin beads remove both anionic and cationic ions 28 29 that have passed through the first two chambers (6, Ions removed in the mixed exchange chamber (9) 30 pass through the relevant ion exchange membranes (7, 31 10) to the single exchange chambers, where they, as 32

8

well as ions exchanged therein, pass through the 1 relevant ion exchange membranes into the electrode 2 3 compartments. 4 From the mixed chamber (9) final product water (21) 5 6 is obtained for use. 7 The electrode compartments (2, 15) are flushed with 8 water to elute the ions from the system as 9 concentrate (22). This flow may be in series or in 10 parallel. 11 12 In an alternative arrangement, feed water could 13 firstly be passed into the cation exchange chamber 14 (12), followed by the anion exchange chamber (6), 15 before being passed into the mixed exchange chamber 16 This alternative flow-path arrangement also 17 allows the removal of precipitative cations such as 18 calcium before they reach the anion exchange 19 material (8) and anion membranes (4, 7) on which 20 they are likely to precipitate. As these ions pass 21 into the cathode exchange chamber (12), it is 22 preferable to maintain a low pH in the cathode 23 exchange chamber (12) and to feed the cathode 24 chamber (15) with water, or acid, devoid of 25 precipitative ions. 26 27 The product water (21) exiting the mixed exchange 28 chamber (9) of the present invention has been found 29 to be of low ionic content. Indeed, the flow rate 30 and purification achieved by the present invention 31 is comparable with prior art EDI apparatus, which 32

9

1 generally involves a significantly more complex 2 arrangement of chambers. 3 4 In another arrangement of the present invention, the 5 feed water (18) is pre-mixed with a proportion of 6 already purified water (21). By diluting the load 7 (i.e. concentration of impure ions to be removed 8 from the water), a higher flow rate through the apparatus can be achieved. 10 11 Indeed, a ratio of 10:1 of already purified water:impure water allows a flow rate of at least 12 13 2/3 litres per minute through the apparatus shown in 14 Figure 1. The already purified water could be 15 supplied from a separate source, or be re-circulated product water (21) from the present apparatus. 16 17 18 The following test data using a design of stack as 19 shown in Figure 1 confirms the benefit of the 20 present invention: 21 22 Example 1 23 24 A stack with internal plate dimensions 150 mm x 66 25 mm x 15 mm was operated on a blend of reverse 26 osmosis permeate and deionised water. With a feed 27 of conductivity 18.2 μ S/cm (adjusted to 25°c) the stack purified 0.55 litres per minute to a 28 conductivity of 0.073 μ S/cm when a current of 1.3 29 30 amps was applied between the electrodes. With a 31 feed of 7.2 µS/cm, 1.37 litres per minute were 32 purified to 0.092 μ S/cm at 1.3 amps.

10

1	Example 2
2	
3	A stack with dimensions 135 mm \times 68 mm \times 10 mm was
4	operated recirculating from a tank. Water was
5	intermittently taken off after the stack and extra
6	make up was fed to the stack from a reverse osmosis
7	membrane. The applied current was 3.16 amps. When
8	the reverse osmosis unit was operating the feed to
9	the stack was 12.5 $\mu S/cm$ and this was purified at a
10	rate of 1.95 litres per minute to 0.062 $\mu S/cm$. When
1.1	recirculating from the tank the feedwater reduced in
12	conductivity to 0.32 μ S/cm at which time the product
13	water was 0.057 μS/cm.
14	
15	The present invention incorporates advantages of
16	both separate resin bed and mixed resin bed
17	technology. Separate resin beds are beneficial for
18	removing known amounts of defined ionic impurity
19	types, both anion and cation, and the current
20	passing through that resin bed can be utilised in
21	removing solely that type of ion.
22	
23	If the feed water is first passed through a cation
24	exchange resin bed, cations can be removed from the
25	solution causing a reduction in the solution pH.
26	Similarly, an anion resin bed will increase the pH.
27	Changes in pH help to prevent bacterial growth, and
28	may also be used to prevent precipitation, or
29	increase the ionic nature of weakly charged species
30	

11

1 Meanwhile, mixed resin beds have been noted to 2 handle high flow rates of water whilst still 3 achieving high levels of purification. 4 5 The present invention has several further 6 advantages. It provides a compact purification unit 7 using a single set of electrodes. It is of simple 8 form, allowing simplified manufacturing thereof, 9 with less complication and therefore with reduced 10 risk of potential breakdown. 11 As mentioned before, water may be passed through 12 13 each chamber independently, allowing different flow 14 rates, including no flow, at different times. 15 16 Also, the number of chambers of the present 17 invention, possibly being only five, are less than 18 many prior art apparatus, thus reducing the problems 19 of back pressure on the feed water, and allowing a 20 faster flow rate therethrough. The use of 21 relatively thick chambers in the present invention 22 also reduces the feed water back pressure. 23 24 Furthermore, feed water through the present 25 invention does not pass through the anode or cathode 26 chambers as occurs in some prior art apparatus, 27 thereby avoiding the problem of gas in the product 28 water. 29 30 Also, the present invention aids removal of weakly ionised species, and can be used in a manner to 31 inhibit precipitative fouling. 32

WO 02/04357

12

PCT/GB01/02967

1	Clai	
	Clai	<u>IMS</u>
2		
3	1.	An electrodeionisation apparatus comprising,
4		successively:
5		
6		means defining an anode chamber,
7		means defining one or more anion exchange
8		chambers,
9		means defining one or more mixed exchange
LO		chambers,
11		means defining one or more cation exchange
12		chambers, and
13		means defining a cathode chamber,
14		·
15		the anion, mixed and cation exchange chambers
16		providing a flow path for water to be purified.
17		•
18	2.	Apparatus as claimed in Claim 1 involving one
19		anion exchange chamber and one cation exchange
20		chamber.
21		
22	3.	Apparatus as claimed in Claim 1 or Claim 2
23		wherein two or more of the chambers are divided
24		by perm-selective membranes.
25		•
26	.4.	Apparatus as claimed in Claim 3 wherein any
27	•	membrane located between the or each central
28		mixed exchange chamber and the cathode chamber
29		is a cation membrane.
30		·
31	5.	Apparatus as claimed in Claim 3 or Claim 4
32		wherein any membrane located between the or

1		each mixed exchange chamber and the anode
2		chamber is an anion membrane.
3		
4	6.	Apparatus as claimed in any one of the
5		preceding Claims wherein the or each anion
6		exchange chamber partly, substantially of
7		wholly contains anion exchange material.
8		•
9	7.	Apparatus as claimed in any one of the
LÖ		preceding Claims wherein the or each cation
11		exchange chamber partly, substantially or
12		wholly contains cation exchange material.
13		
L 4	8.	Apparatus as claimed in any one of the
15		preceding Claims wherein the anode chamber
16		partly, substantially or wholly contains ion
17	•	exchange material.
18		
19	9.	Apparatus as claimed in any one of the
20		preceding Claims wherein the cathode chamber,
21		partly, substantially or wholly contains ion
22		exchange material.
23		
24	10.	Apparatus as claimed in Claim 8 or Claim 9
25		wherein the ion exchange material is cation
26		exchange material.
27	•	
28	11.	Apparatus as claimed in any one of the
29		preceding Claims wherein the or each mixed
30		exchange chamber partly, substantially or
31		wholly contains mixed ion exchange material.

WO 02/04357

14

PCT/GB01/02967

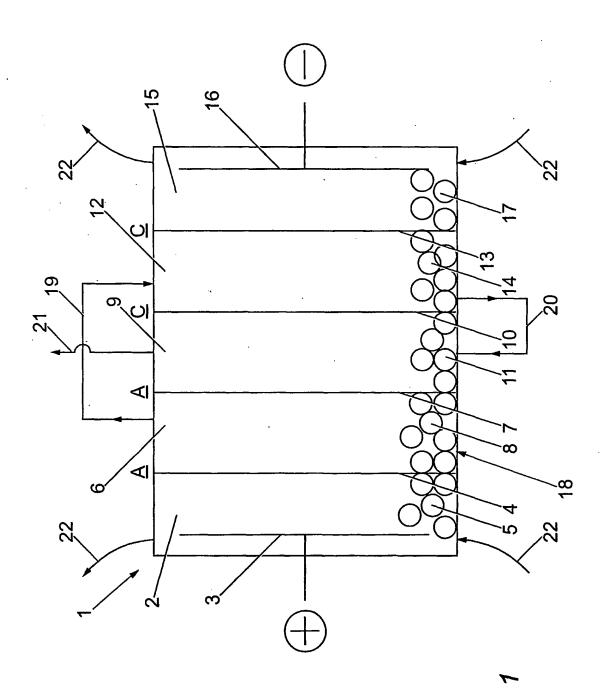
1	12.	Apparatus as claimed in any one of Claims 6 to
2		11 wherein the ion exchange material is resin
3		beads.
4		
5	13.	Apparatus as claimed in any one of the
6		preceding Claims wherein the or each anion,
7		cation and/or mixed exchange chambers are
8		between 5-20mm wide.
9		
10	14.	A method of electrodeionisation comprising
11		causing or allowing water to be purified to
12		flow through an anion exchange chamber
13		neighbouring an anode chamber, followed by flow
14		through a cation exchange chamber neighbouring
15		a cathode chamber, followed by flow through a
16		mixed exchange chamber located between the
17		anion exchange chamber and the cation exchange
18		chamber.
19		
20	15.	A method of electrodeionisation comprising
21		causing or allowing water to be purified to
22		flow through a cation exchange chamber
23		neighbouring a cathode chamber, followed by
24		flow through an anion exchange chamber
25		neighbouring an anode chamber, followed by flo
26		through a mixed exchange chamber located
27		between the anion exchange chamber and the
28		cation exchange chamber.
29		
30	16.	A method as claimed in Claim 14 or claim 15
31		wherein the flow of water through each chamber
32		is independent of other flows.

WO 02/04357

15

PCT/GB01/02967

1 17. A method as claimed in any one of Claims 14 to 2 Claim 16 wherein the anode and cathode chambers 3 are flushed with a desalting stream. 4 5 A method as claimed in any one of Claims 14 to 18. 17 which involves two or more anion exchange 6 7 chambers and/or two or more cation exchange chambers and/or two or more mixed exchange 8 9 chambers, wherein the water to be purified 10 flows through one or more subsequent anion 11 exchange chambers and/or one or more subsequent 12 cation exchange chambers and/or one or more 13. subsequent mixed exchange chambers in the same 14 or any suitable or relevant order. 15 16 A method as claimed in any one of Claims 14 to 19. 17 18 wherein the water to be purified is combined with purified water prior to 18 19 electrodeionisation. 20 21 A method as claimed in Claim 19 wherein the 20. 22 water to be purified is combined with water 23 provided by outflow product of the method of 24 Claims 14 to 18. 25 26 21. A method as claimed in any one of Claims 14 to 27 20 wherein apparatus as claimed in any one of 28 Claims 1 to 13 is used.



INTERNATIONAL SEARCH REPORT

Inte inal Application No PC 1/4B 01/02967

A. CLASSIF	CO2F1/469 B01D61/48 B01J47/08	8	
	International Patent Classification (IPC) or to both national classification	ion and IPC	
B. FIELDS S	SEARCHED cumentation searched (classification system followed by classification	n symbols)	
IPC 7	C02F B01D B01J		
Documental	ion searched other than minimum documentation to the extent that su	ich documents are included in the helds se	arched .
Electronic da	ata base consulted during the international search (name of data bas	e and, where practical, search terms used	
WPI Dat	ta, PAJ, EPO-Internal		
	ENTS CONSIDERED TO BE RELEVANT		Deleverable delevable
Category *	Citation of document, with indication, where appropriate, of the rele	vant passages	Relevant to claim No.
А	DE 32 38 280 A (LIEBER HANS WILHE DR IN) 19 April 1984 (1984-04-19) claims 1-3,5; figures 1,2,5		1-21
Ā	GB 2 311 999 A (ELGA GROUP SERVIC 15 October 1997 (1997-10-15) cited in the application claims 1,5; figure 1	ES LTD)	1-21
A	US 4 687 561 A (KUNZ GERHARD) 18 August 1987 (1987-08-18) cited in the application claim 1.16; figure 1		1-21
A	US 3 869 376 A (TEJEDA ALVARO R) 4 March 1975 (1975-03-04) figure 5		1-21
Furti	her documents are listed in the continuation of box C.	Palent family members are listed	in annex.
° Special ca	tegories of cited documents :	'T' later document published after the inte	mational filing date
consid	ent defining the general state of the art which is not lered to be of particular relevance	or priority date and not in conflict with cited to understand the principle or the invention	eory underlying the
filing d	ale	"X" document of particular relevance; the cannot be considered novel or cannot	be considered to
which	ni which may throw doubts on priorily claim(s) or is clied to establish the publication date of another n or other special reason (as specified)	involve an inventive step when the do "Y" document of particular relevance; the cannot be considered to involve an in	taimed Invention
O docum	ent referring to an oral disclosure, use, exhibition or means	document is combined with one or mo ments, such combination being obvious	ore other such docu-
P docume later ti	ent published prior to the international filing date but nan the priority date claimed	in the art. *8* document member of the same patent	family
Date of the	actual completion of the international search	Date of mailing of the International ser	arch report
2	6 October 2001	12/11/2001	
Name and	malling address of the ISA	Authorized officer	
	European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tet. (+31-70) 340-3040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Borello, E	

INTERNATIONAL SEARCH REPORT

formation on patent family members

inte nal Application No PCT7GB 01/02967

Patent document cited in search report		Publication date		Patent family member(s)	Publication date
DE 3238280	Α	19-04-1984	DE	3238280 A1	19-04-1984
GB 2311999	Α	15-10-1997	DE	19713977 Al	30-10-1997
US 4687561	Α	18-08-1987	DE	3217990 A1	17-11-1983
			DE	3241681 A1	17-05-1984
			DE	3241682 Al	17-05-1984
			ΑT	63479 T	15-06-1991
			AU	1557783 A	02-12-1983
			DE	3382286 D1	20-06-1991
			WO	8303984 A1	24-11-1983
			EP	0113387 A1	18-07-1984
			CA	1289103 A1	17-09-1991
US 3869376	Α	04-03-1975	NONE		